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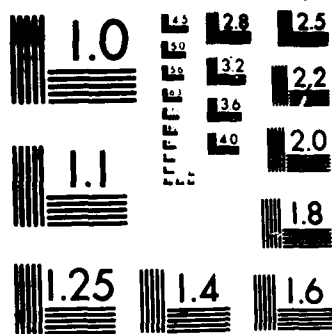
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An XPS Study of the Composition of Thin  
Polyimide Films Formed by Vapor Deposition

by

R. N. Lamb<sup>+</sup>, J. Baxter, M. Grunze, C. W. Kong and W. N. Unertl

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FINAL VERSION

AN XPS STUDY OF THE COMPOSITION OF THIN POLYIMIDE FILMS FORMED  
BY VAPOR DEPOSITION

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ABSTRACT

Films of polyimide ( $> 8\text{nm}$ ) were formed on a polycrystalline silver surface following heating of a vapor deposited layer of 4,4' oxydianiline (ODA) and 1,2,4,5 Benzenetetracarboxylic anhydride (PMDA). The imidization reaction leading to polymer formation was followed in situ with X-ray Photoelectron Spectroscopy. The uncertainties inherent in a quantitative analysis of the composition of the top 8 nm surface layer (corresponding to the sampling depth of the technique) are discussed with respect to thick films of ODA and PMDA adsorbed on a clean Cu(111) surface at 200 K. The fully cured polyimide film contains excess ODA-like and PMDA-like constituents as trapped molecules or terminal groups.

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Polyimide is an important polymer for application in solid state electronic technology because of its favorable dielectric properties and high thermal stability. In this paper we describe X-ray Photoelectron Spectroscopy (XPS) measurements of polyimide films deposited onto clean copper and silver substrates. These films were formed by co-deposition of 1,2,4,5 benzenetetracarboxylic anhydride (PMDA) and 4,4 oxydianiline (ODA) from the vapor phase, followed by imidization in ultra-high vacuum to form polyimide films with thicknesses greater than ~10 nm. We have also used this method to form ultra-thin films with thicknesses as small as about 1 nm. The properties of these and the polyimide-substrate interface are described elsewhere [1,2]. The polyimide films examined in this paper are thick enough so that the polyimide-substrate interface is not probed by XPS. The results are characteristic of the mean-properties of the outer 5-10 nm of the films.

Figure 1 shows the reaction pathway. PMDA and ODA react to form the intermediate polyamic acid (PAA). Heating to  $T > 200^{\circ}\text{C}$  causes imidization to occur, resulting in the release of water and the formation of polyimide chains. The numbers associated with each carbon in Fig. 1 will be used in parentheses throughout this paper to avoid possible ambiguities in the discussion of the results.

In this article we also summarize our XPS results on the thermal stability of thick vapor deposited films of pure PMDA and ODA and demonstrate some of the ambiguities which influence evaluation of stoichiometries from x-ray photoemission data. A fuller account of the adsorption and decomposition behavior of ODA and PMDA will be given elsewhere [2].

## 1. EXPERIMENTAL

The organic vapor sources consisted of small quartz test tubes containing crystalline PMDA and ODA (Aldrich Gold Label). Care was taken to minimize hydrolysis of PMDA during charging of the source. Each tube was heated by passing current through a tantalum wire wrapped around its outside. Temperatures were measured by type K thermocouples inserted through the mouth of each tube. In the range 348-383 K thick layers of pure PMDA or ODA or thick co-deposited layers could be formed in times on the order of 10-20 minutes on copper and 2-5 minutes on silver. No effort was made to maintain a stoichiometric mixture of PMDA and ODA vapor fluxes during the co-deposition experiments. It was found, however, that the composition of the thick polyimide films were nearly independent of the precise deposition conditions.

The copper and silver substrates were cleaned by argon ion sputtering and heating in hydrogen and oxygen, respectively. The copper samples had no detectable impurities and the silver sample had a small amount of residual oxide. The clean, polycrystalline copper and silver samples were held at room temperature or lower during the deposition. The sticking coefficient of PMDA and ODA on a Cu{111} single crystal was found to be substantially lower than on polycrystalline copper at room temperature and thick films could only be formed by cooling the crystal to a temperature of 200 K. No differences in stoichiometry were found between the thick polyimide films formed on these various substrates.

The samples had surface areas of about 1-2 cm<sup>2</sup> and were mounted on a manipulator which allowed them to be translated from the XPS analysis chamber into a side chamber for deposition. The side chamber contained the PMDA and ODA sources and a quadrupole mass analyzer. The total pressure was about 10<sup>-6</sup> mbar during deposition.

The XPS instrument contained a Leybold-Heraeus EA11 hemispherical electrostatic electron energy analyzer. Analysis was made with Mg  $K_{\alpha}$  radiation at 100 watts. The experimental resolution was measured to be 0.92 eV using the Ag 3d emission. The electron binding energies were calibrated against the Au 4f<sub>7/2</sub> emission at  $E_B = 84$  eV.

## 2. RESULTS

In Fig. 2 we show the C 1s, O 1s, and N 1s spectra of thick condensed films of ODA and PMDA on a Cu{111} sample at 200 K. The film thicknesses are in excess of 8 nm, i.e. the substrate photoemission signal was completely attenuated as for the polyimide films discussed below. Shifts in C 1s, O 1s and N 1s binding energy ( $\sim 0.7$  eV) with increasing coverage (starting with submonolayer deposits) were observed for the ODA, indicating that charging effects up to the film thicknesses used in Fig. 2 are important. No change in the PMDA binding energies with increasing thickness was observed [2].

The spectral features are best discussed with reference to the chemical formula for ODA and PMDA shown in Fig. 1.

The two carbon 1s bands of PMDA at  $E_B = 286.3$  eV and  $E_B = 290.2$  eV in Fig. 2(a) are easily identified as arising from the phenyl carbon atoms (1) and the carbonyl carbon atoms (2) respectively. On the high binding energy side of the carbonyl band additional intensity is observed. Since this high binding energy shoulder grows in parallel to the main features, we exclude the presence of carbon atoms in chemical environments other than in undissociated PMDA and instead suggest that the intensity is due to final state effects ("shake-ups") in the photoemission process.

The C 1s spectra of ODA, Fig. 2(a), consists of an unresolved doublet with maxima at 285.5 and 286.5 eV. The unresolved doublet



structure is due to the two non-equivalent types of carbon in the phenyl rings of the ODA labelled (3) and (4). The electron withdrawing properties of the central ether oxygen atom and the amino nitrogen atoms resulting in a 1 eV increase in the binding energy of carbon atoms (4). As for PMDA, intensity due to final state effects in the photoemission process are observed at  $E_B > 290$  eV.

The corresponding O 1s spectra, shown in Fig. 2(b), can be interpreted accordingly. For ODA a single O 1s band from the ether oxygen is observed at 534.4 eV. The PMDA O1s spectrum shows an unresolved doublet, due to the carbonyl oxygen atoms ( $E_B \sim 533$  eV) and the anhydride oxygen atoms ( $E_B \sim 534$  eV). Around  $E_B \sim 539$  eV a small band due to final state effects is observed.

The N 1s band of ODA, Fig. 2(c), has a single, symmetric band centered around 400.5 eV.

In Figs. 3-5 we show the XPS spectra for layers of ODA and PMDA co-deposited at room temperature on a polycrystalline silver substrate. Figure 3 shows the C 1s spectra of the room temperature deposited layer (a) and the changes occurring during subsequent heating. Comparison with Fig. 2(a) shows that, clearly, spectrum (a) cannot be explained simply as a mixture of PMDA and ODA, but indicates that a chemical reaction has occurred between the two molecules. Comparison with published XPS data for polyamic acid [3,4] suggests that a large fraction of the two molecules must have reacted to form polyamic acid, the polyimide precursor. Characteristic for the C 1s spectrum of polyamic acid is the broad and ill defined emission between 288.7 and 291.7 eV from the carbonyl carbon atoms, which are in a variety of chemical environments in PAA. With heating, imidization of the polyamic acid takes place. The carbonyl carbon peak at 288.8 eV emerges and sharpens during annealing while the single peak at about 286.2 eV splits. The resulting

C 1s spectrum is very similar to that for spin coated polyimide films [3]. Our spectra indicate that the imidization process is complete after heating the sample to ~550 K (Spectra 3d).

Figure 4 shows the O 1s spectra corresponding to the sequence of C 1s spectra discussed above. The oxygen 1s spectra of PAA has a strong band around 533.7 eV, which is identified as due to hydroxyl groups in the polyimide precursor. Consistent with the general reaction scheme, heating leads to imidization and loss of hydroxyl groups as water and consequently to a disappearance of the O 1s hydroxyl band. The final spectra (e) then is due primarily to the different oxygen species in polyimide.

The N 1s emission for this experiment is shown in Figure 5 together with the N 1s of a thick ODA film for comparison. The initial deposit has at least two components as expected for a PAA intermediate in coexistence with unreacted ODA. Following heating, Fig. 5f, the N 1s emission consists of a main peak centered at 400.6 eV plus a shoulder extending to lower binding energies. Pure polyimide would have only a single peak due to the nitrogen in the t-amine. The shoulder is indicative of a mixed film which contains more than just polyimide.

### 3. SEMI-QUANTITATIVE ANALYSIS OF THE XPS DATA

Semi-quantitative estimates of composition, types of chemical bonding and film thickness can be extracted from the XPS data. The relative intensities of the C 1s, N 1s and O 1s transitions are related to the relative compositions of the films. The shape of each XPS emission band is determined by the distribution of bonding environments. Attenuation of the substrate XPS signals provides a measure of the mean thicknesses during deposition of the adsorbate overlayers. This section outlines the methods used to extract these quantities from the data. A critical

evaluation of the analysis for the data in Figs. 2-5 will be given in the next section.

### 3.1. Film Composition

If the adsorbate film is assumed to be isotropic and homogeneous, the XPS core level intensity ( $I$ ) due to element  $X$  is [5]:

$$I_X \propto \sigma_X N_X \Gamma(E) T(E) \quad (1)$$

for films thick enough to totally attenuate the substrate emission, where  $\sigma$  is the photoelectron excitation cross section,  $N$  is the number of  $X$  atoms per unit area,  $\Gamma(E)$  is the electron mean free pathlength at kinetic energy  $E$ , and  $T(E)$  is the energy dependent part of the spectrometer transmission function. In the case of a single monolayer, electron attenuation is not important and Eq. (1) has the form

$$I_X \propto \sigma_X N_X T(E) . \quad (2)$$

Therefore, relative compositions of two elements can be obtained from the measured core level intensities using (1):

$$\frac{N_1}{N_2} = \frac{I_1}{I_2} \frac{\sigma_2}{\sigma_1} \frac{\Gamma_2}{\Gamma_1} \frac{T_2}{T_1} \quad (3)$$

for the case of thick films and by

$$\frac{N_1}{N_2} = \frac{I_1}{I_2} \frac{\sigma_2}{\sigma_1} \frac{T_2}{T_1} \quad (4)$$

for the case of thin films.

The relative cross sections ( $\sigma$ ) were taken from the calculations of Scofield [6] with respect to the C 1s cross section,  $\sigma_{C1s} = 100$ . The N 1s value is  $\sigma_{N1s} = 177$  and the O 1s value is  $\sigma_{O1s} = 285$ .

The energy dependence of the electron spectrometer used in this study was determined from the measured silver and copper XPS intensity variations in the constant  $\Delta E$  and constant  $\Delta E/E$  modes as described by Seah and Anthony [7]. Its form in the constant  $\Delta E$  mode is

$$T(E) \propto E^{-0.73} \quad (5)$$

where  $E$  is the kinetic energy of the XPS transition.

A compilation of electron mean-free path lengths for organic materials by Seah and Dench [8] shows that measured values of  $\Gamma$  lie between 0.8 and 9.0 nm over the range of kinetic energies of interest here (700-1000 eV). They suggest the following expression for  $\Gamma$  ( $E > 150$  eV):

$$\Gamma(\text{nm}) = 110 \frac{E^m}{\mu} \quad (6)$$

where  $m$  is assumed to be 0.5,  $E$  is in electron volts, and  $\mu$  is the density in  $\text{kg/m}^3$ . For polyimide  $\mu = 1.41 - 1.43 \times 10^3 \text{ kg/m}^3$  [9]. Equation 6, however, has a very large root-mean-square uncertainty of  $\pm 1.5$  nm. Other values of  $m = 0.66$  [10] and  $m = 0.71$  [11] have been suggested.

Combining these values for  $\sigma$ ,  $\Gamma$  and  $T$  into Eq. (3) for thick films produces

$$\frac{N_1}{N_2} = \frac{I_1}{I_2} \frac{\sigma_2}{\sigma_1} \left[ \frac{E_2}{E_1} \right]^{m-0.73} \quad (7)$$

where  $0.5 < m < 0.71$ . Accordingly, eq. (4) for a monolayer becomes

$$\frac{N_1}{N_2} = \frac{I_1}{I_2} \frac{\sigma_2}{\sigma_1} \left[ \frac{E_2}{E_1} \right]^{-0.73} \quad (8)$$

### 3.2. Lineshape Analysis

The XPS lineshapes contain information about the distribution of bonding environments of the atoms in the films. However, for complex samples such as those studied in this paper, it is difficult to carry out an unambiguous analysis. Firstly, there are multiple binding states. For example, there are six symmetry inequivalent carbon bonding states in pure polyimide. Thus, the C 1s emission contains six contributions each of which can in principle have a different binding energy. Secondly, in the case of thin films there can be multiple environments. Here, emission from atoms located near the metallic substrate will be more strongly screened by metal conduction electrons than emission from atoms within the bulk of the film. Thus, each of the binding energy components of the C 1s lineshape can occur over a range of energies. Thirdly, final state effects can cause the emission from a single bonding state to have several peaks. Finally, heterogeneities in the sample can introduce additional contributions. For example, the composition near the vacuum and substrate interfaces can be different from that in the bulk or the polyimide films may contain unreacted or fragmented ODA or PMDA. The polyimide might also have a high density of terminal groups or branching points which would introduce local compositional heterogeneities. The combinations possible in these instances may lead to a vast range of atom ratios in the resulting films. Some of these

are summarized in Table 1. It is expected that contributions from a number of these limiting examples may be present.

For these reasons, a unique analysis of the data is not possible without additional information. Therefore, we have used the interpretation of C 1s lineshapes proposed for bulk polyimide films by Silverman et al. [12] as a guide to analysis of our vapor deposited films. They show that the low binding energy peak (284.8 eV) is due to the phenyl carbons (3) in the ODA portion (Fig. 1). The high binding energy peak (288.7 eV) is due to carbonyl carbons (2). The remaining peak at about 286 eV is attributed to the remaining carbons (1) and (4) in Fig. 1. The ODA ether carbons (4) are thought to be about 0.4 eV more tightly bound than the PMDA phenyl carbons. In our analysis we have neglected this 0.4 eV splitting.

Fits to the measured lineshapes were made in the following way: The number of peaks to be fit to the data and their approximate binding energies were chosen. All peaks were constrained to have the same FWHM and the background was assumed to be linear over the energy range of the fit. The locations, heights and widths of the peaks and the height and slope of the background were then adjusted to give the best least squares fit to the data.

### 3.3. Film Thickness

Attenuation of the Ag 3d intensity was used to estimate the effective thickness of the adsorbate films. For the case of a homogeneous isotropic film with uniform thickness  $d$

$$I = I_0 e^{-d/\Gamma} \quad (9)$$

where  $\Gamma$  is the mean-free pathlength of Ag 3d photoelectrons in the overlayer and  $I_0$  and  $I$  are the Ag 3d intensities measured at the clean and film covered surface, respectively.

Thickness estimates based on Eq. (9) are crude for several reasons. First, the value of  $\Gamma$  is uncertain as discussed above. For example,  $\Gamma$  calculated from Eq. (6) varies between 0.9 and 3.9 nm for various choices of  $m$ . Other authors have quoted higher values for saturated organic films [14] but suggest that increasing aromaticity will produce smaller path lengths. The values of  $d$  quoted in this paper were obtained assuming  $\Gamma = 12 \text{ \AA}$  for a homogeneous overlayer [15]. With this  $\Gamma$ , films thicker than about 7.5 nm totally attenuate the substrate signal.

Thicknesses estimated from Eq. (9) will also be in error if the adsorbate layer has non-uniform thickness. In this case, the measured intensity will be determined predominantly by the thinnest regions of the film so that the effective thickness  $d$  calculated from Eq. (9) will have a value between the average thickness and the smallest thickness.

#### 4. DISCUSSION

##### 4.1 Thick PMDA and Thick ODA Films

We first discuss the XPS data for the thick condensed layers of pure ODA and PMDA shown in Fig. 2. The uncertainties which arise in determination of stoichiometries from XPS data center around the accuracy in determining the variables in Eq. 7. Since the photoionization cross sections ( $\sigma$ ) and kinetic energies ( $E_K$ ) are essentially fixed, the choice of  $m$  and the measurement of the peak areas ( $I$ ) will be the main contributors to any errors in analysis of stoichiometry.

The range of  $m$  reflects the experimental variations found in the electron mean free paths ( $\Gamma(E)$ ) of the constituents within the film. As discussed in the previous section this has been reported with values

between  $0.5 < m < 0.71$ . Such a variation produces no more than a 5% change in stoichiometries.

In contrast, the procedures associated with the assignment of peaks and the subsequent determination of their areas are less easily defined. The main uncertainties arise not so much in the absolute area measurement but how to include the shake-up features and how to precisely subtract the background due to inelastic scattering. Since the former essentially "borrows" intensity from the main peaks, the comparison between various ratios of the same atoms in the different chemical environments is not clear cut. On the other hand comparison of different atom ratios must include these shakeups. A closer look at the PMDA and ODA film analysis illustrates the uncertainties.

The C 1s and O 1s spectra for PMDA and ODA, Figs. 2(a) and 2(b), include lines used by us to define the inelastic background and the separation of the shake-up features from the main peaks. In the case of PMDA, the intensity ratios of the phenyl carbon (1), carbonyl carbon (2) and the shake-up are 6.0:4.0:0.4. If the shake-up intensity is not included, the ratio C(1):C(2) is identical to the stoichiometric value 6:4. Inclusion of the additional intensity with either C(1) or C(2) would change the experimental ratios to a value less consistent with the expected ratio. Thus, in this case, it appears that C(1) and C(2) atoms contribute equally to the shake-up intensity.

Comparison of different atoms within the film does not require this specific determination of the various contributions in the shake-up intensity. Rather the total area includes these. In PMDA the C:O ratio is 10:5.7 irrespective of whether shakeups are included or not. Note however that the stoichiometry differs slightly from the 10:6 ratio expected from pure PMDA. Similarly the evaluation of stoichiometry for the thick ODA layer including shake-up intensity gives a ratio of C:O:N



of 12:1.2:2.3 which varies slightly from that of the 12:1:2 expected. These deviations from expected stoichiometry highlight the difficulties in defining the correct inelastic electron background. This gives rise to an intrinsic error in the stoichiometric ratios of approximately  $\pm 0.25$  with respect to the amount of oxygen and nitrogen relative to the total carbon content. We note, however, that a possible anisotropy in the films, i.e. a preferential stacking of the molecules, could also lead to deviations of the experimental stoichiometry values from those expected for homogeneous materials.

#### 4.2. Thick Polyimide Films

The mean composition of the thick co-deposited PMDA/ODA films determined from the data in Figs. 3-5 as a function of temperature were determined using Eq. 7. The upper panel in Fig. 6 displays the results for the stoichiometric ratios of carbon to oxygen to nitrogen (normalized to 22 carbon atoms per polyamic acid or polyimide repeat unit) and the lower panel displays nitrogen to total oxygen, hydroxyl oxygen and carbonyl carbon normalized to 2 nitrogen atoms in PAA or PI. In all cases the shake-up intensities have been considered in the total stoichiometry ratios and the total C 1s shake-up band has been included in the carbonyl C 1s intensity in the lower panel. The amount of hydroxyl oxygen was determined by subtracting the normalized polyimide oxygen 1s spectra, Fig. 4(e) from Figs. 4a-d. For each annealing temperature, both the stoichiometry determined from Eq. 7 for the thick film limit ( $m = 0.73$ ) and the thin film limit, Eq. 8, are displayed by the higher and lower symbol respectively for each element. The difference between these two values corresponds also to the estimated error involved in defining the inelastic electronic background.

The overall picture presented in the top panel suggests that stoichiometric ratios of C:O:N for polyimide are produced following

heating in excess of 700° K. At lower temperatures the deviations indicate the transition from a co-deposited film made up primarily of polyamic acid (PAA) to that of polyimide (PI). The subtleties associated with these changes are plotted in the bottom panel of Fig. 6. The choice of N:O:C(2):OH reflects the specific chemistry of the imidization reaction as well as indicating any excess of unreacted PMDA and/or ODA.

Initial deposition should lead to total ratios of C:O:N = 22:7:2 comparable with polyamic acid. This C:O:N ratio for a stoichiometric film of PAA is not found experimentally. There is an apparent deficiency of oxygen coupled with an excess of nitrogen (upper panel) and a marked decrease in carbonyl C(2) and total oxygen (lower panel) from that of a pure stoichiometric film of PAA where N:O:C(2):OH = 2:7:4:2. These results indicate an excess of ODA and simply highlights the lack of accurate control of the individual fluxes of the constituents during vapor deposition.

With increasing temperature the most obvious feature is the decrease and final disappearance of the hydroxyl oxygen intensity. This is due to the condensation and subsequent elimination of water during imidization. Accompanying it is the appearance of nearly stoichiometric ratios of N:C (2) ~ (2:4) and total C:O ~ (22:5) for polyimide; both of which remain essentially constant throughout the ensuing heating regime. An excess of nitrogen with respect to total carbon (upper panel) and a deficit of oxygen with respect to nitrogen (lower panel) remains up to ~640 K suggesting excess ODA. These results, however, rule out a model of a polyimide film with only excess ODA, since such a situation would lead to a deficit of oxygen with respect to total carbon and a deficit of carbonyl carbon with respect to nitrogen. The simplest plausible explanation of the stoichiometry results postulates that both unreacted ODA and PMDA or ODA and PMDA terminal groups are trapped in the cured

film. Such a composition of the film would be consistent with a nearly stoichiometric carbon to oxygen ratio, but an excess of nitrogen. The nearly stoichiometric ratio between nitrogen and carbonyl carbon might be due to the fact that the complete shake-up intensity in the C 1s spectra, which by our procedure for background subtraction amounts to about 45% of the carbonyl C 1s peaks, have been included in the evaluation of the N:C(2) ratio. If besides  $\pi - \pi^*$  transitions in the carbonyl moiety similar transition associated with the phenyl carbon system contribute to the shake-up intensity, the amount of carbonyl carbon will be overestimated.

To complete the analysis we shall examine the lineshape of the C 1s, O 1s, and N 1s emission with respect to the mean composition of a polyimide film cured at 570 K for 30 min. Fig. 7 shows the best fits to the lineshapes with the numbers on the figure indicating the relative (percentage) intensities of the components.

Pure polyimide would have only a single N 1s peak due to the imide nitrogen. The small component at lower binding energy demonstrates that two types of nitrogen are present. This supports the presence of excess ODA-like units as discussed above where nitrogen is in the form of primary or secondary amine. The N intensity ratio indicates about one excess ODA per three polyimide structural units.

Since ODA contains only ether oxygen the O 1s component at 533.3 eV will be increased relative to the 532 eV component. The fit in Fig. 7 shows that this is indeed the case although the increase in relative intensities would require nearly equal amounts of ODA and polyimide, which however is not consistent with the nearly stoichiometric total carbon to oxygen ratio of 22:5.4.

Since ODA has no carbonyl carbons, excess ODA will not contribute to the 290.1 eV component of the C 1s line in Fig. 7a. The intensity of

the carbonyl band is approximately consistent with the total stoichiometry, when the shake-up features are included in the C(2) intensity. That this procedure indeed overestimates the total carbonyl content is born out by the carbonyl to ODA ether O 1s intensity in Fig. 7c. As stated above, the O 1s peak suggests a deficit of carbonyl oxygen compared to ether oxygen which is larger than can be explained by excess ODA alone. Thus, the relative photoemission intensities for the various functional groups suggest that the film has a deficiency of carbonyl groups, even when excess ODA is included in the analysis. This result confirms our assumption that the shake-up intensity in the C 1s spectra does not originate from carbonyl groups only.

Curing the film to 720 K leads to a nearly stoichiometric composition as shown in Fig. 6. However, like the film cured at 570 K (discussed above) the lineshape of the N 1s and O 1s peaks (Figs. 4e and 5f respectively) are also not consistent with a pure polyimide film.

We conclude that the fully cured films must have significant heterogeneities in composition within the sampling depth of x-ray photoelectron spectroscopy. A possible heterogeneity consistent with the measurements is an excess of ODA and a deficiency of carbonyl groups which could occur if the PMDA units release carbonyl groups and are thus partially fragmented. This fragmentation could be constrained to the PI surface, or could be a general property of the films. Certainly there are numerous other possibilities for discussing the results once fragmentation is included in the analysis. We feel however that the present data provides insufficient constraints to meaningfully test these more complex possibilities. Additional data using such techniques as infrared absorption spectroscopy or high-resolution electron energy loss spectroscopy are needed.

## 5. SUMMARY

Thin polyimide films have been grown by imidization of co-deposited PMDA/ODA films. ODA and PMDA react within the film to form polyamic acid. The polyamic acid releases water upon heating above about 390 K and converts to polyimide. Excess PMDA and ODA is released.

Analysis of XPS spectra indicate the fully cured polyimide film contains excess ODA-like and PMDA-like constituents perhaps as trapped molecules or as terminal groups. A deficit of carbonyl groups indicate that the films may also contain PMDA fragments which have lost carbonyl groups.

## 6. ACKNOWLEDGEMENTS

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**REFERENCES**

1. M. Grunze and R. N. Lamb, Chem. Phys. Letts. 133 (1987) 283.
2. R. N. Lamb, W. N. Unertl and M. Grunze (in preparation).
3. H. J. Leary and D. S. Campbell in "Photon, Electron and Ion Probes of Polymer Structure and Properties," Ed. D.W. Dwight, T. J. Fabish and H.R. Thomas, A.C.S. Symp. Ser. 16 (1981) 419.
4. J. R. Salem, F. O. Sequeda, J. Duran, W. Y. Lee and R. M. Yang, J. Vac. Sci. Technol. A4 (1986) 369.
5. M. P. Seah in "Practical Surface Analysis," Ed. D. Briggs and M. P. Seah (Wiley, New York) (1983) 181.
6. J. H. Scofield, J. Electron. Spectros., 8 (1976) 129.
7. M. P. Seah and M. T. Anthony, Surf. Interface Anal. 6 (1984) 230.
8. M. P. Seah and W. A. Dench, Surf. Interface Anal. 1 (1979) 2.
9. H. Dressler and S. N. Holter in "Encyclopedia of Chemical Technology," Ed. Kirk-Othmer (Wiley, New York) (1982) 705.
10. C. D. Wagner, L. E. Davis and W. M. Riggs, Surf. Interface Anal. 2 (1980) 53.
11. D. R. Penn, J. Electron. Spectrosc. 9 (1976) 40.
12. B. D. Silverman, P. N. Sanda and P. S. Ho, J. of Polym. Sci., Polym. Chem. 23 (1985) 2857.
13. B. D. Silverman, J. W. Bartha, J. G. Clabes, P. S. Ho and A. R. Rossi, J. Polym. Sci. Part A 24 (1986) 3325.
14. E. Cartier, P. Pfluger, J. J. Pireaux and M. Rei Vilar, App. Phys. A (in press).
15. D. T. Clark in "Encyclopedia of Chemical Technology," Ed. W. Dekeyser and D. Reidel, (Dordrecht) 1973.

**TABLE CAPTIONS**

Table 1. Deviations from Stoichiometry in the Formation of Polyimide

**FIGURE CAPTIONS**

- Fig. 1. Schematic representation of the reaction of ODA and PMDA to form polyimide. (L = number of completed polymer units, see Table 1)..
- Fig. 2. (a) C 1s spectra of a thick film of vapor deposited ODA and PMDA on Cu{111} at 200 K.  
(b) O 1s spectra of a thick film of vapor deposited ODA and PMDA on Cu{111} at 200 K.  
(c) N 1s spectra of a thick film of vapor deposited ODA and PMDA on Cu{111} at 200 K.
- Fig. 3. C 1s spectra of a co-deposited thick film of ODA and PMDA on polycrystalline Ag. Binding energies have not been corrected for changes in spectrometer work function. This shifts indicated binding energies by 1.3 eV toward lower binding energy.
- (a) Room temperature.  
(b) Heated 370 K for 2 min.  
(c) Heated 390 K for 3.5 hrs.  
(d) Heated 550 K for 2.5 hrs.  
(e) Heated 720 K for 30 min.
- Fig. 4. O 1s spectra of a co-deposited thick film of ODA and PMDA on polycrystalline Ag. Binding energies have not been corrected for changes in spectrometer work function. This shifts indicated binding energies by 1.3 eV toward lower binding energy.
- (a) Room temperature.  
(b) Heated 370 K for 2 min.  
(c) Heated 390 K for 3.5 hrs.  
(d) Heated 550 K for 2.5 hrs.  
(e) Heated 720 K for 30 min.
- Fig. 5. N 1s spectra of a co-deposited thick film of ODA and PMDA on polycrystalline Ag. Note primary amine N 1s from ODA for comparison. Binding energies have not been corrected for changes in spectrometer work function. This shifts indicated binding energies by 1.3 eV toward lower binding energy.
- (a) Room temperature.  
(b) Heated 370 K for 2 min.  
(c) Heated 390 K for 3.5 hrs.  
(d) Heated 550 K for 2.5 hrs.  
(e) Heated 550 K for 34 hrs.  
(f) Heated 720 K for 30 min.

Fig. 6. Upper panel: Total ratios of C:O:N for spectra of co-deposited ODA and PMDA on polycrystalline Ag, normalized to 22 carbon atoms in PAA or PI repeat units.

- O 1s
- ▣ N 1s

Lower panel: Total ratios of N:O:C(2):OH for spectra of co-deposited ODA and PMDA on polycrystalline Ag relative to total nitrogen.

- O 1s (total)
- OH O 1s
- × Carbonyl C 1s

Horizontal lines in both panels correspond to the stoichiometry of pure polyimide.

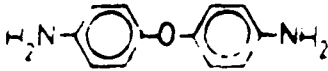
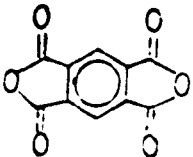

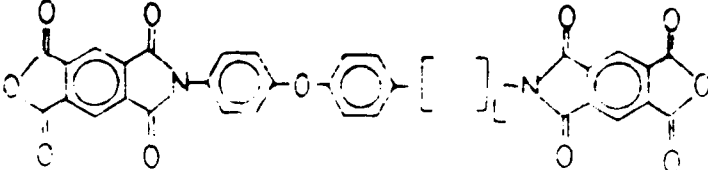
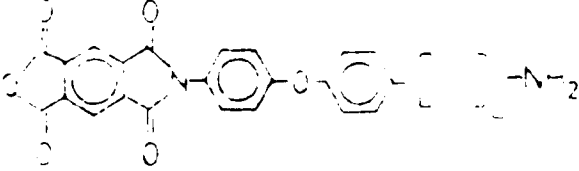
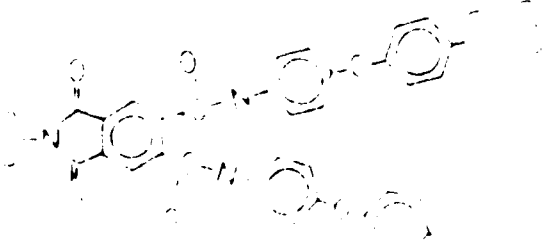
Fig. 7. (a) C 1s spectrum of a thick cured polyimide film on Ag.  
 (b) O 1s spectrum of a thick cured polyimide film on Ag.  
 (c) N 1s spectrum of a thick cured polyimide film on Ag.

Numbers denote percentage intensity of component peaks.



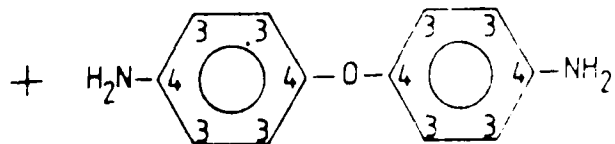
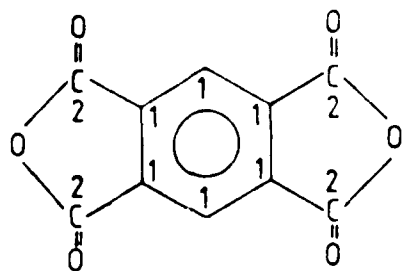
TABLE 1

Deviations from Stoichiometry

Type	Structure	C:N:O L = 10	C:N:O Mean Composition
ODA Impurity		22:2.1:4.8	(22L+12):(2L+2):(5L+1)
PMDA Impurity		22:1.9:5.4	(22L+10):(2L):(5L+6)
ODA Terminal Groups		22:2.1:4.8	(22L+12):(2L+2):(5L+1)
PMDA Terminal Groups		22:1.9:5.4	(22L+10):(2L):(5L+6)
Mixed Terminal Groups		22:2.0:5.1	(22L+22):(2L+2):(5L+6)
Branching		22:2.0:4.85	(22L+34):(2L+3):(5L+6)

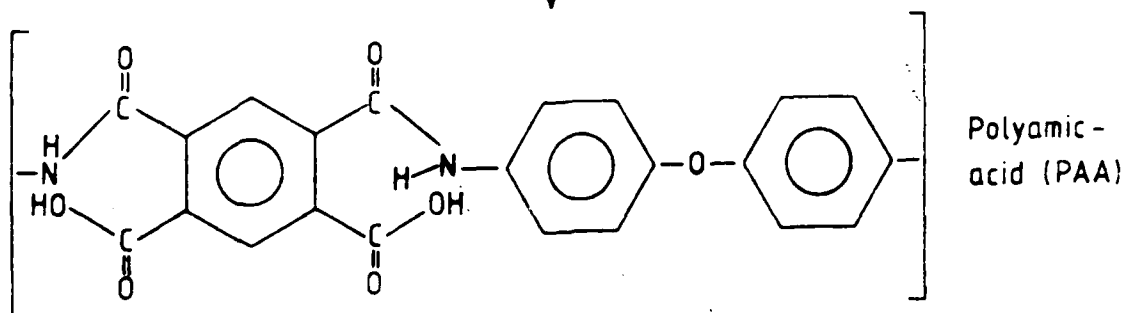
ODA + PMDA

Polyimide



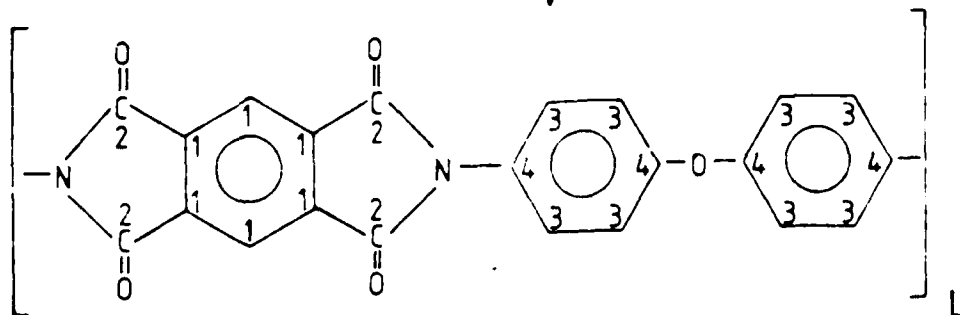
1,2,4,5 Benzenetetracarboxylic  
Anhydride  
PMDA

4,4' Oxydianiline  
ODA



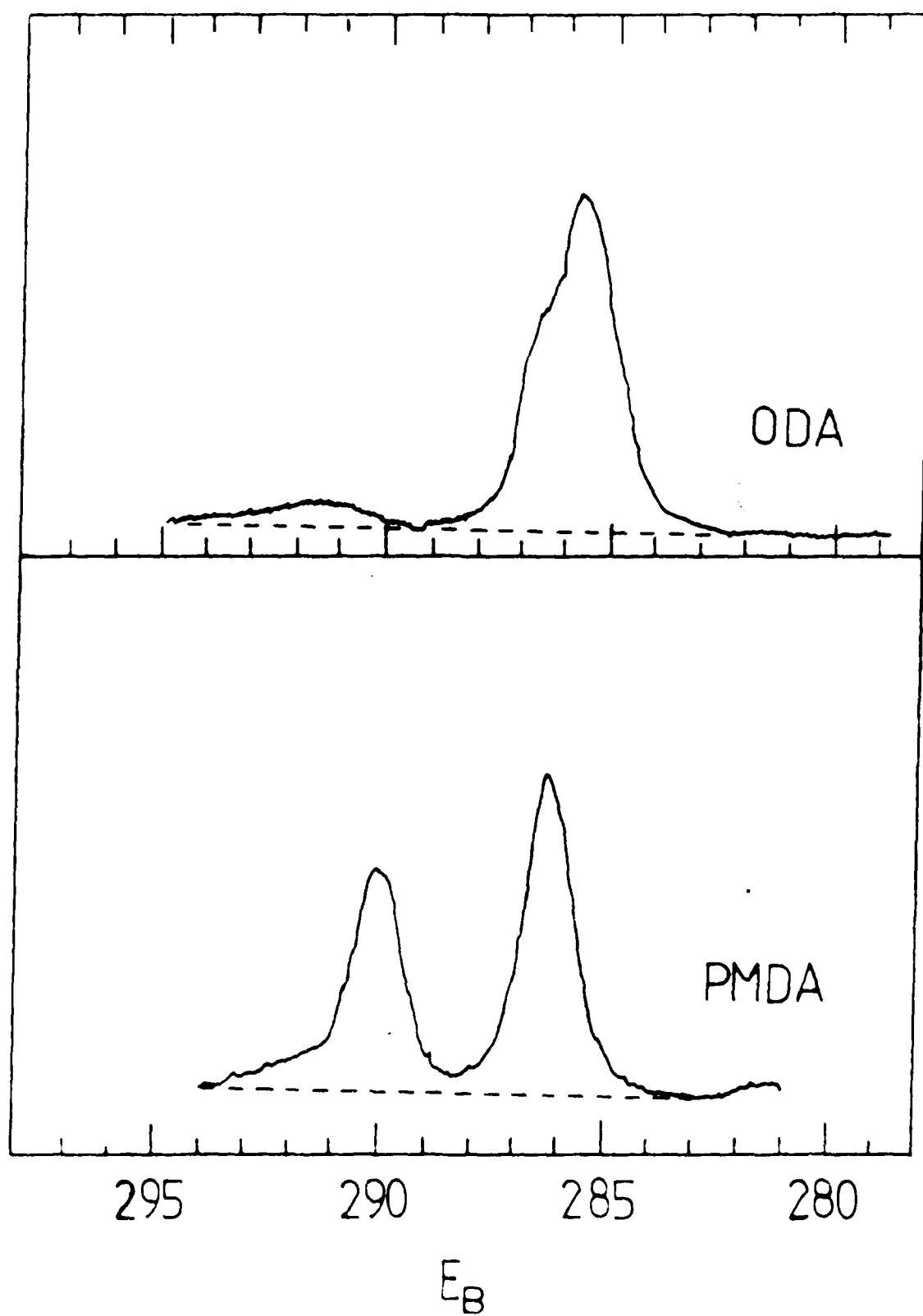
imidization

- H<sub>2</sub>O

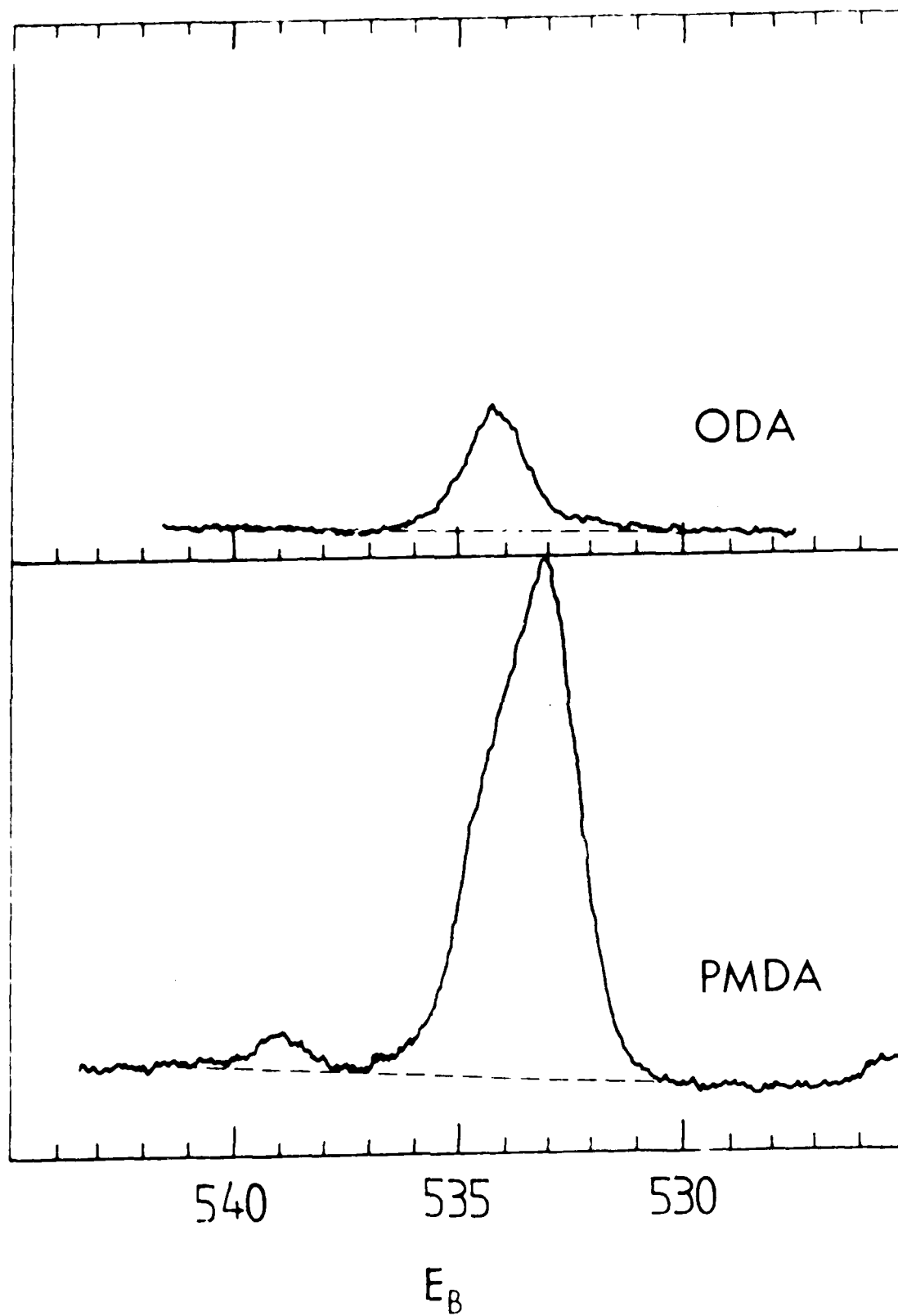


Polyimide (PI)

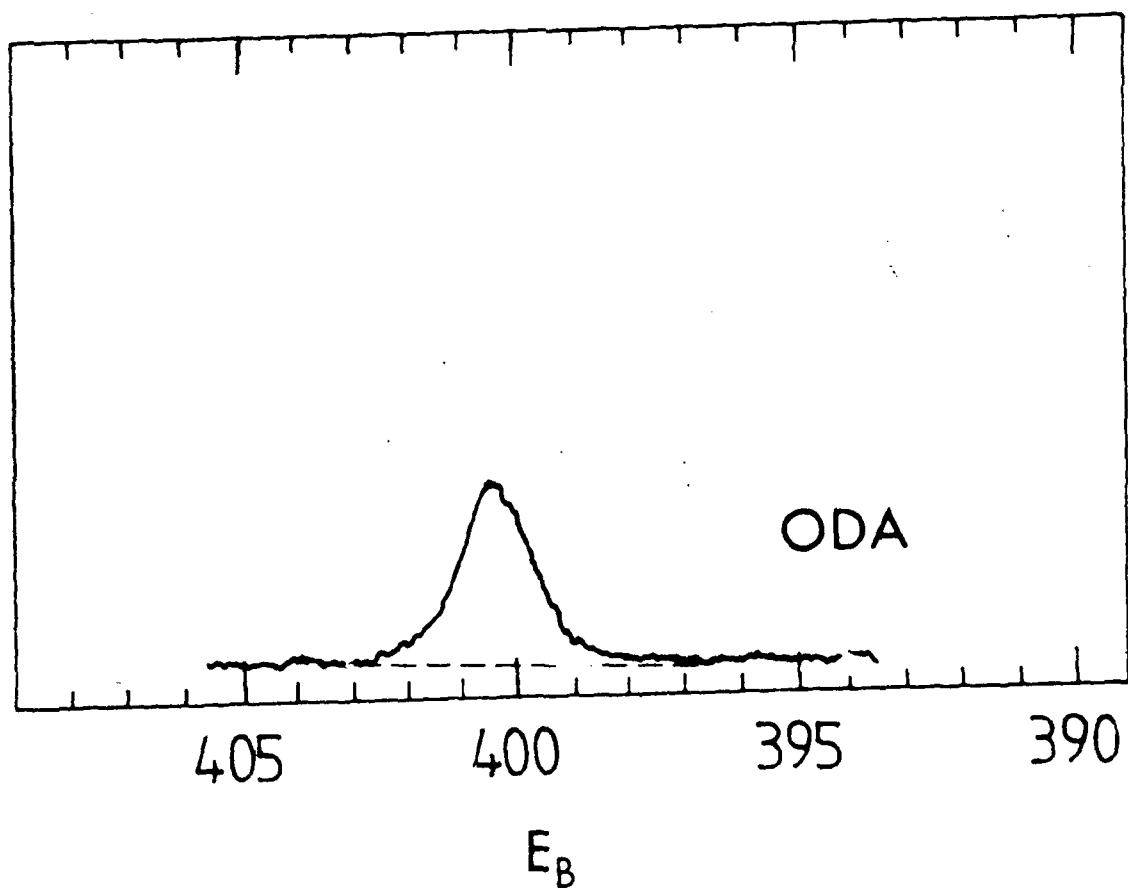
C 1s

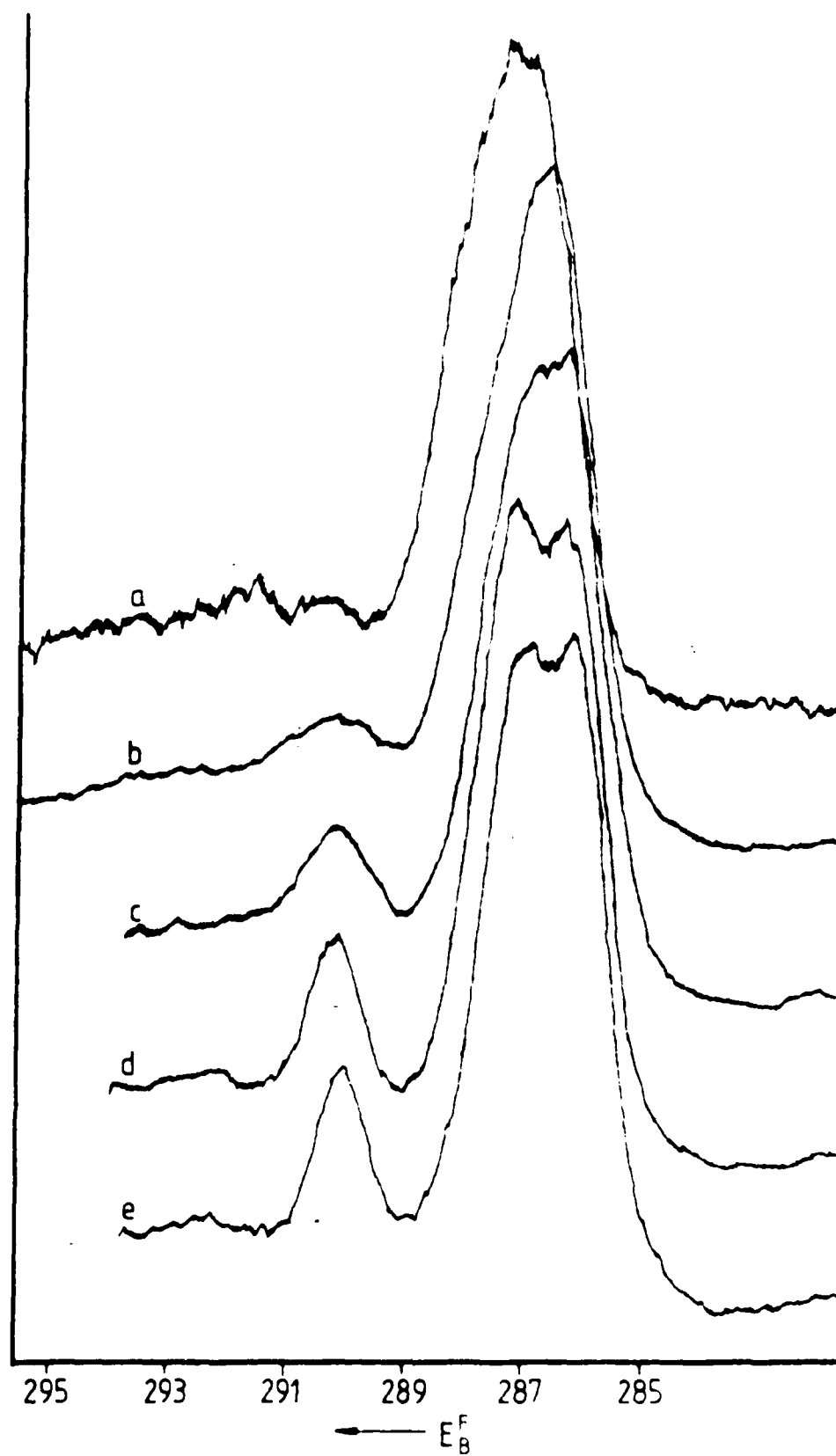


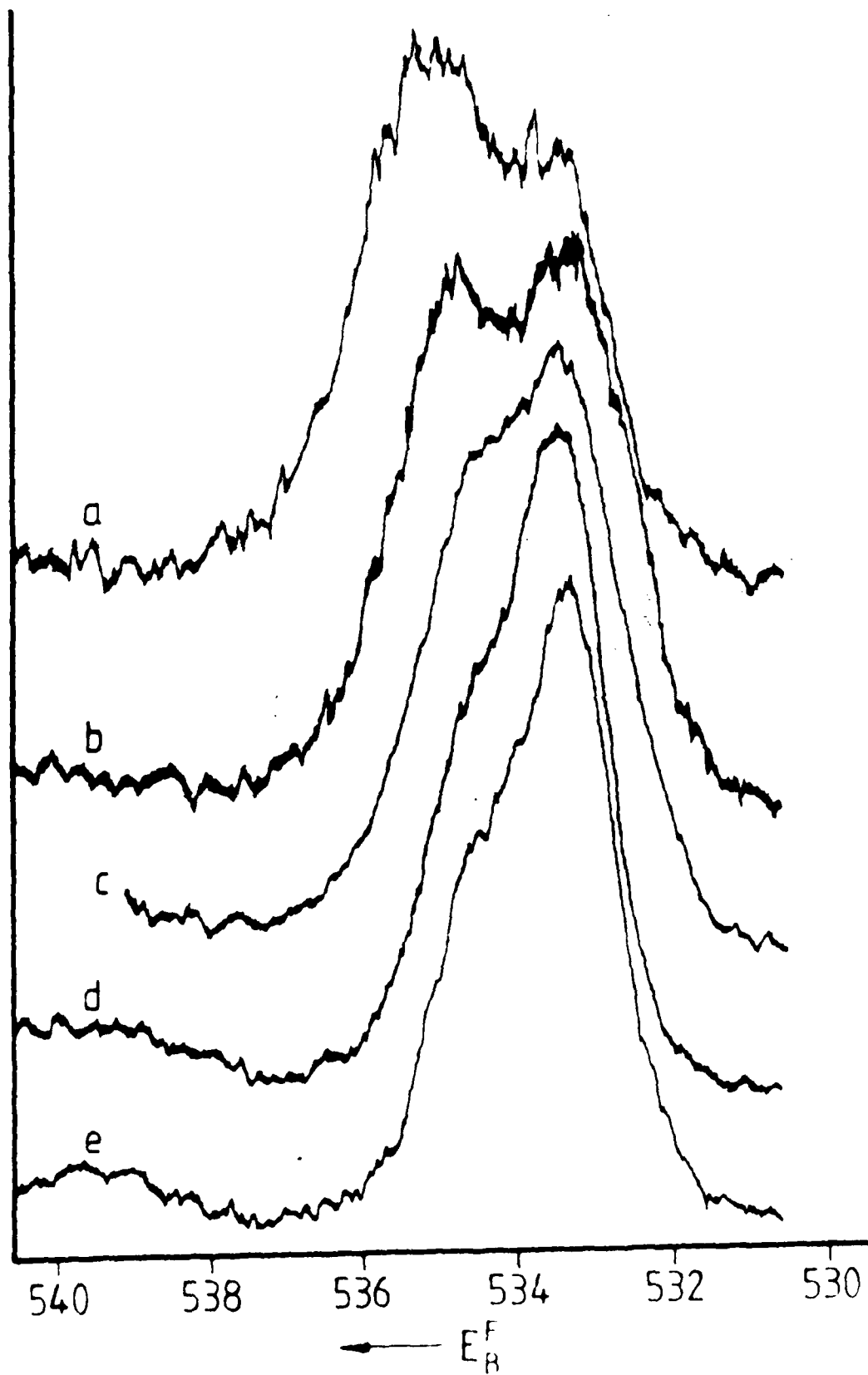
O 1s

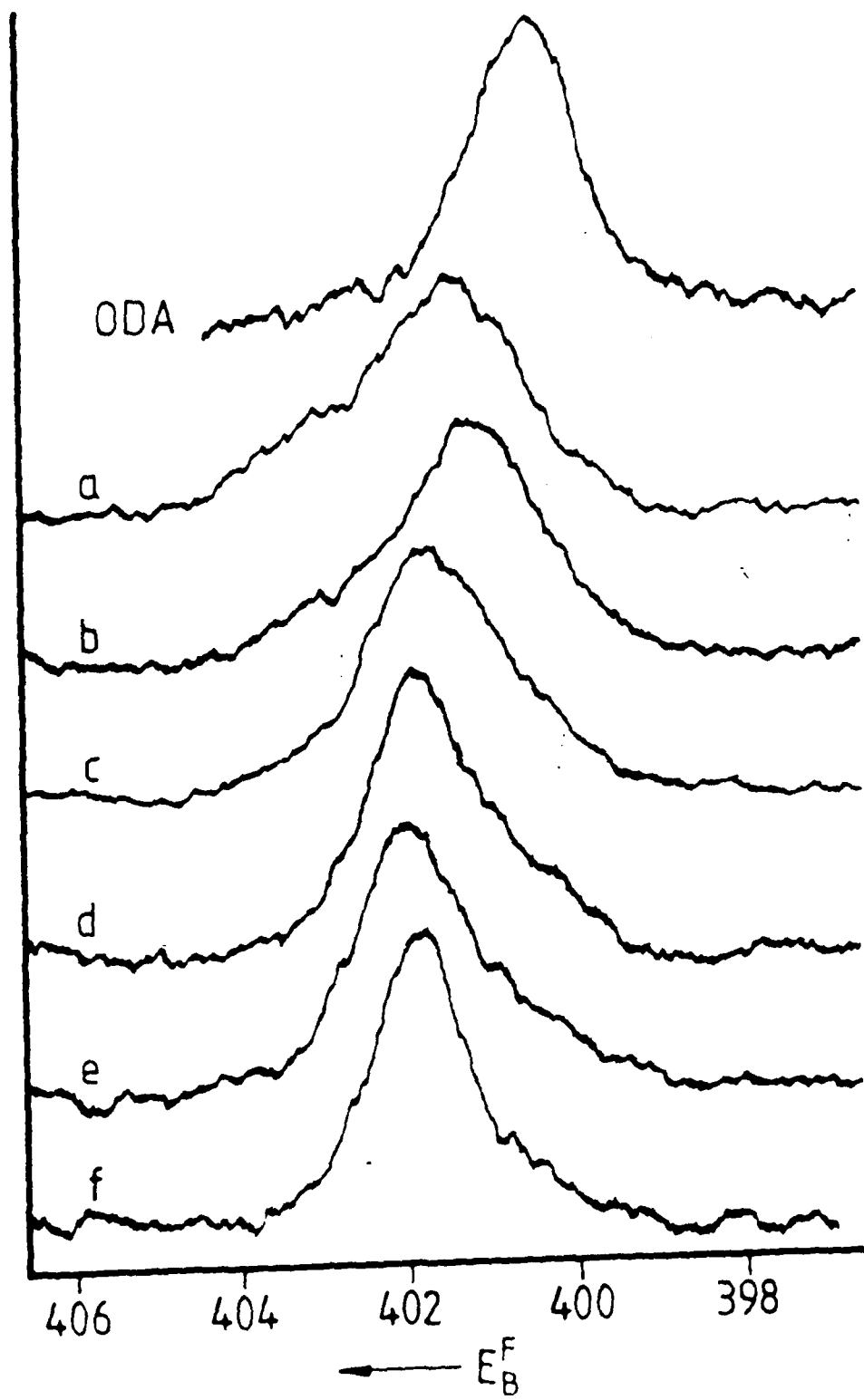


N ls



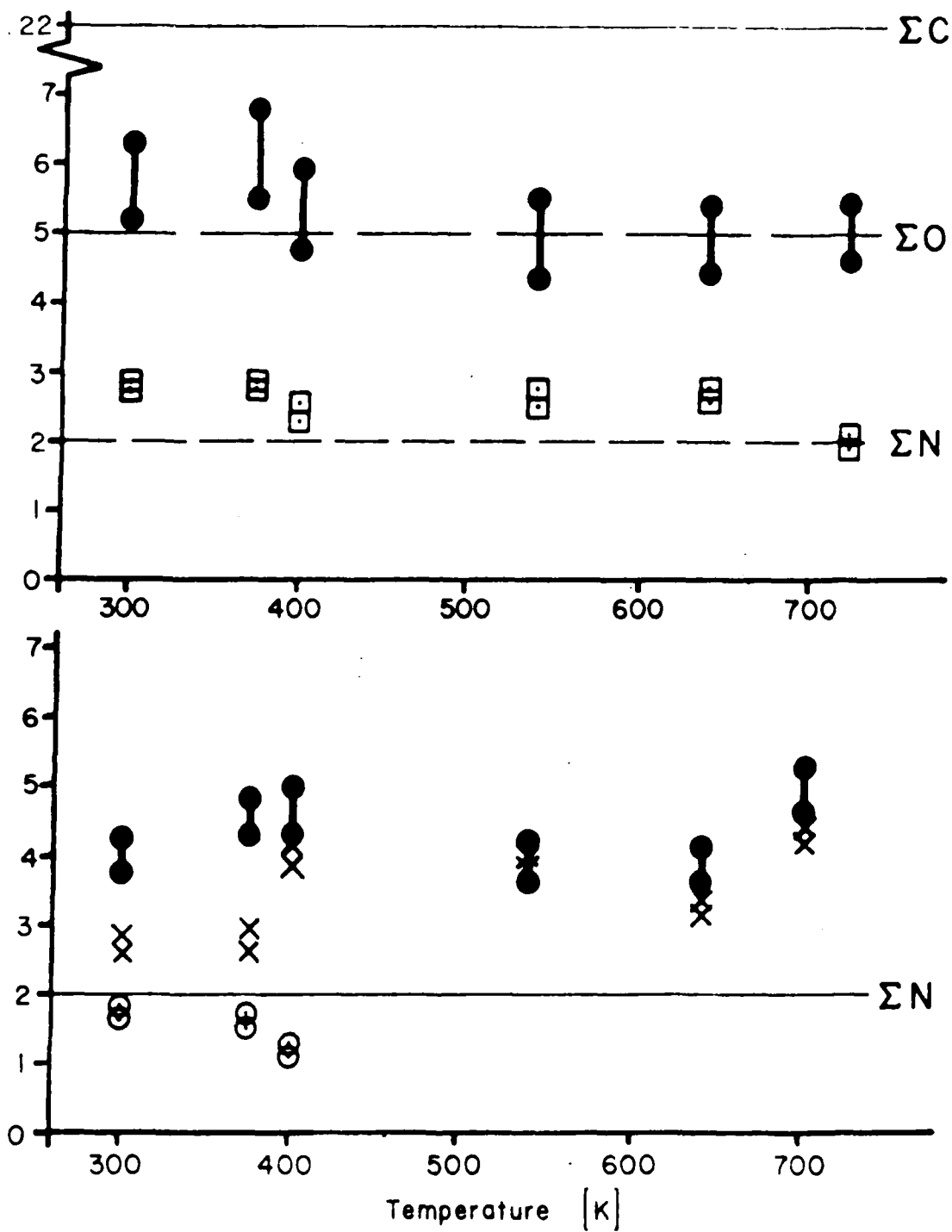


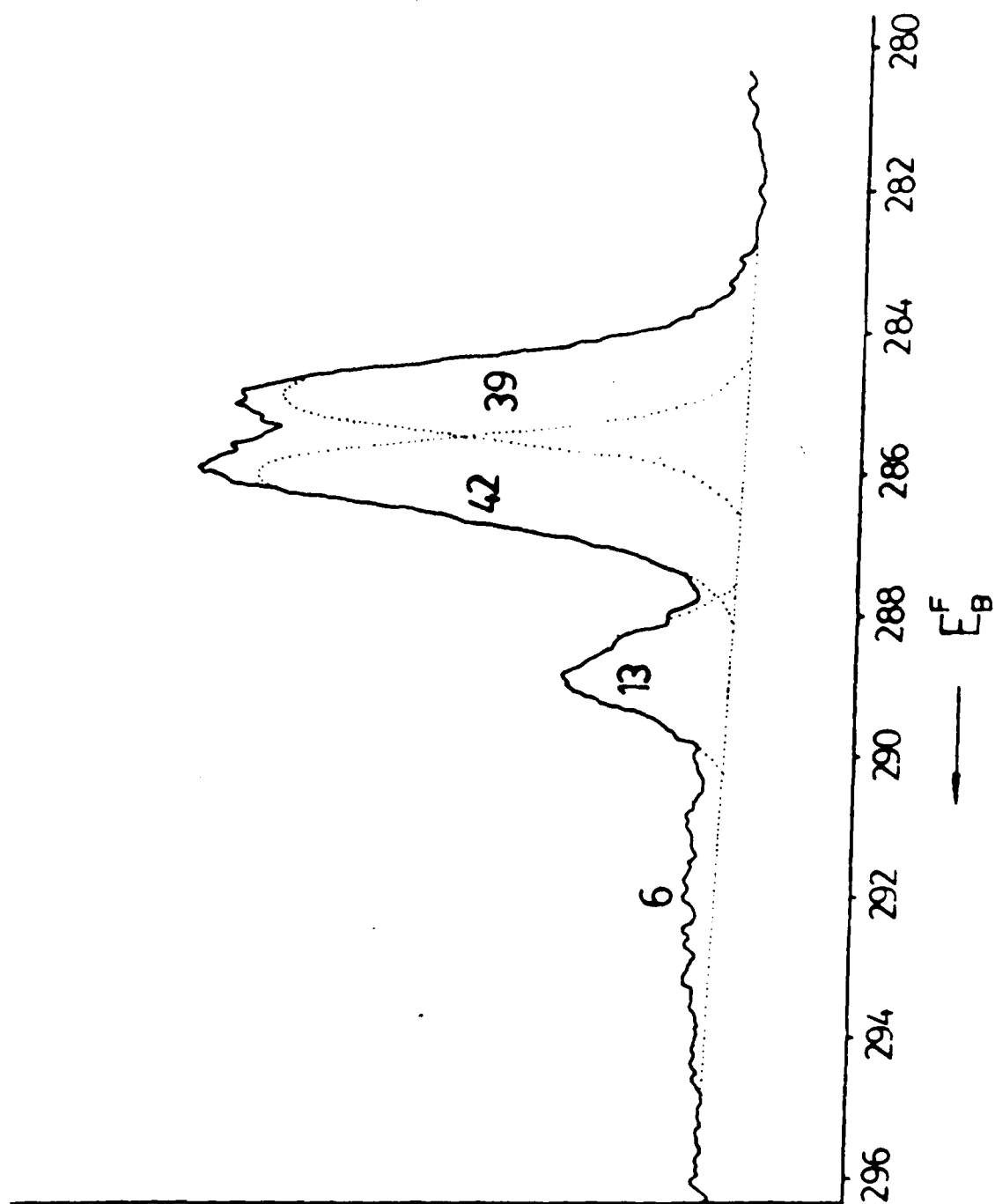




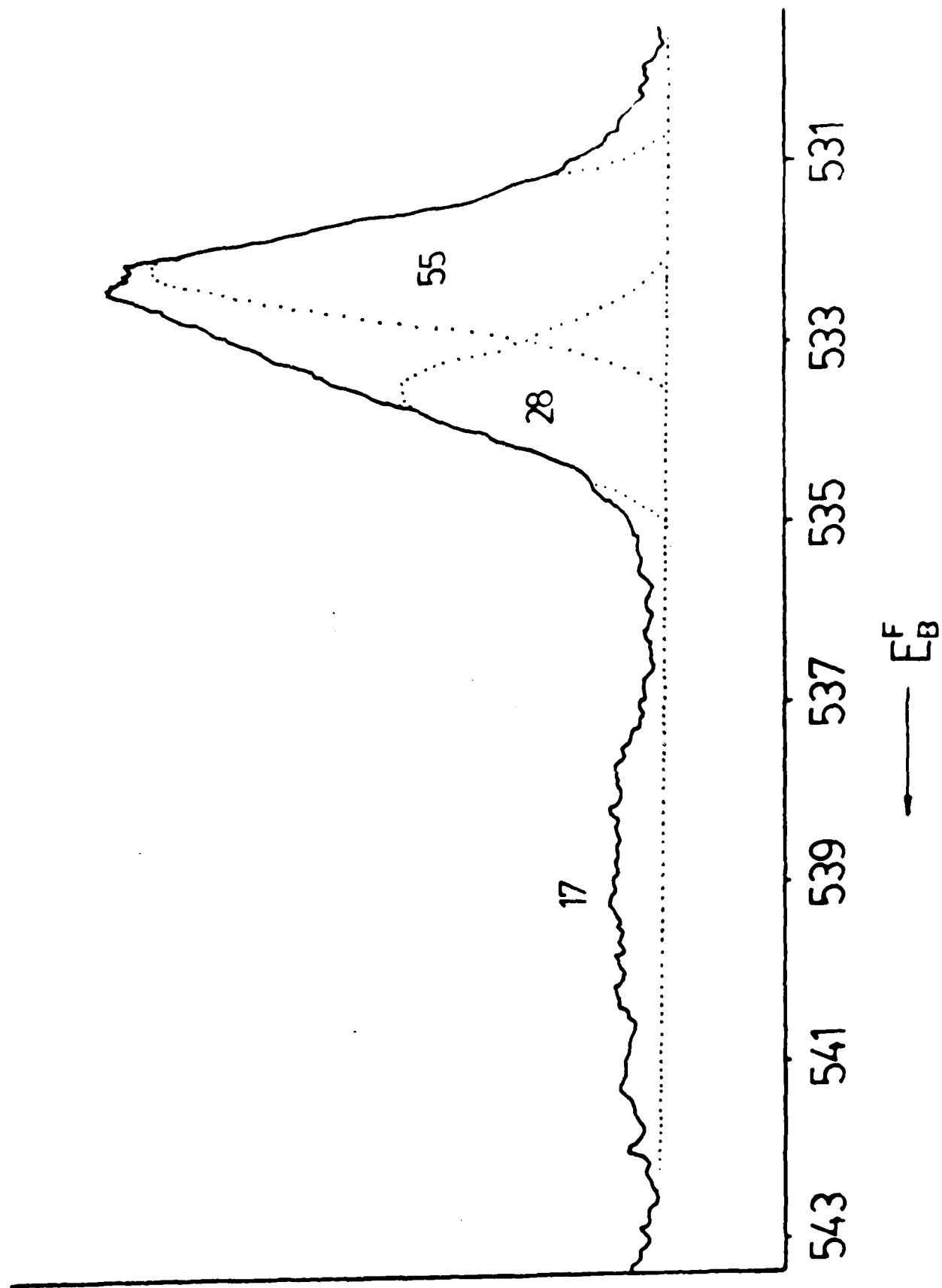


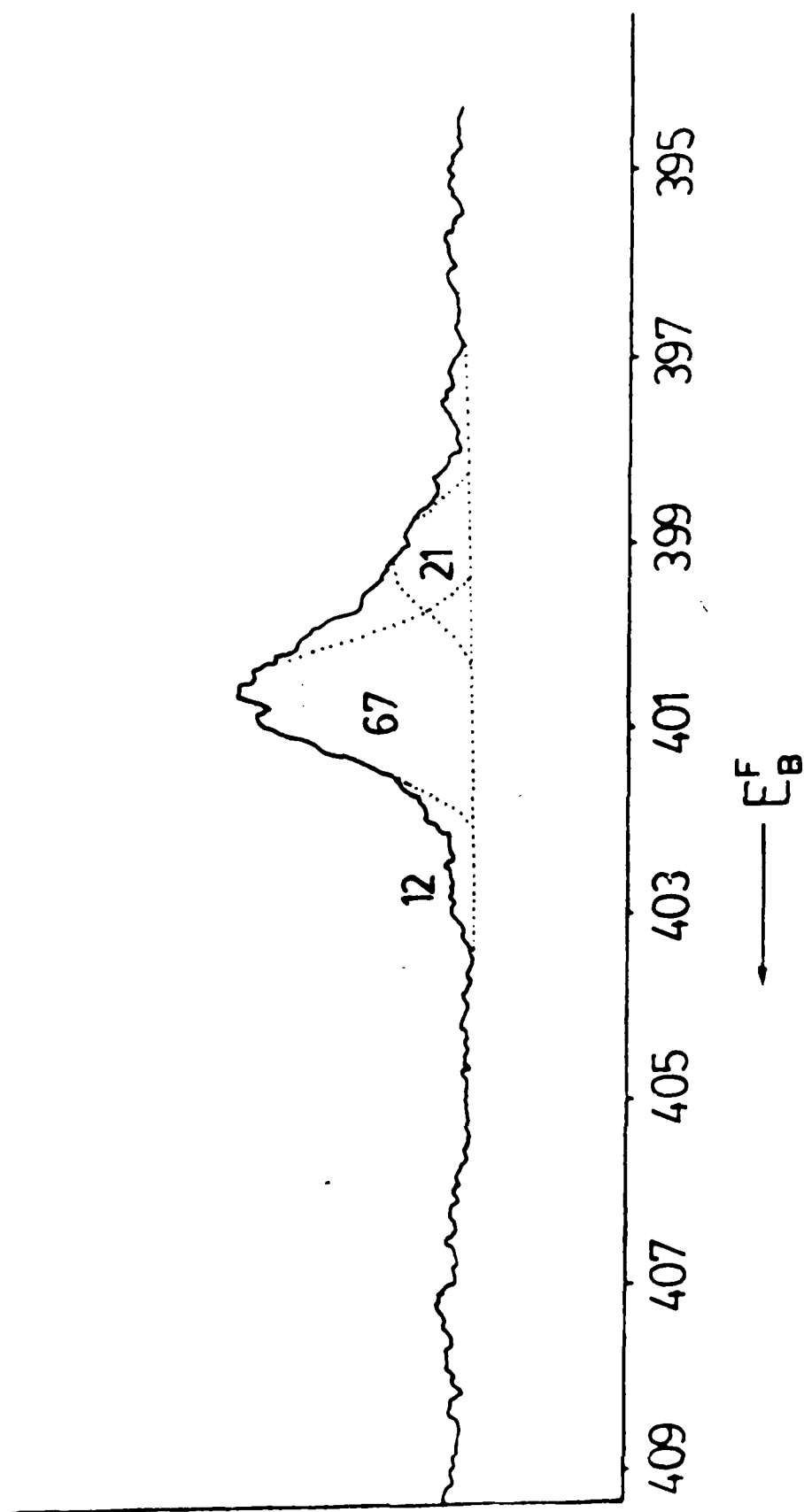
# PI/Ag





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